

A CRITICAL SURVEY OF THE VALUE OF MICROWAVE HEATING FOR THE ACCELERATION OF REACTIONS OF -OH GROUPS IN COAL, AND THE RELATIONSHIP TO NEW ANALYTICAL METHODS FOR -OH DETERMINATION

Parisa Monsef-Mirzai, Harminder Manak and William R. McWhinnie
Department of Chemical Engineering & Applied Chemistry,
Aston University, Aston Triangle, Birmingham B4 7ET

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INTRODUCTION

Research continues into coal utilisation by means which involve chemical reactions, particularly for the production of liquid products. Most of the new processes are based on hydroliquefaction, and for assessment of the suitability of particular coals for this purpose it is desirable to have detailed knowledge of their chemical constitution and reactivity. In respect of the use of coals as chemical feedstocks, as in hydroliquefaction, new classification systems might be desirable based on chemical parameters rather than on carbonisation properties as at present, and here the various functional groups attached to the coal hydrocarbon skeleton would be of great importance.

Functional groups in coals derive from the 'heteroatoms' O, N and S, and of these oxygen is by far the most important, varying regularly with coal rank between about 1 and 15% in British coals. Although -COOH and -CH₃ groups occur in coals of very low rank, oxygen in British coals is distributed between hydroxyl, carbonyl and ether-type groups. The hydroxyl groups, which certainly include phenolic groups, are the most important, and probably provide active reaction sites during hydroliquefaction.

Hydroxyl groups may be detected with reasonable certainty by spectroscopic methods, and can be measured by conversion into derivatives, e.g. by acetylation. Subsequent steps such as hydrolysis, distillation and titration of the recovered acetic acid afford data on -OH content. All such methods are based on heterogeneous reaction processes and there may be residual doubt as to whether the reactions have progressed to equilibrium. Indeed, a method dependent scatter of results is seen in the literature.

The ability of microwave heating to greatly accelerate chemical reactions is now well established.¹ The reaction mixture is typically contained in a microwave transparent Teflon bomb and the rate acceleration is achieved via an Arrhenius effect due to the superheating of the solvent. For this to be possible, it is necessary that the solvent is polar since non-polar materials will not interact with the microwave field. Following testing of a wide range of polar solvents we have found that acetonitrile is the best choice. This is because it superheats rapidly and extracts the minimum amount of the more labile components of coal under the experimental conditions employed. GC/MS analysis of the limited amount of material extracted reveals that oxygen containing materials constitute a negligible quantity of the extract. When the appropriate reagents are sufficiently soluble in acetonitrile, mixed solvents may be used as long as one is a microwave "receptor" e.g. acetonitrile/toluene. For polar reagents, e.g. transition metal salts, water is very appropriate. Of particular interest is that the method is excellent for the acceleration of a range of heterogeneous reactions.² In this presentation we outline the applications of microwave heating for driving coal -OH derivitisation reactions. We point out both advantages and drawbacks of the method.

Methodology

A known weight (0.5 - 1.0 g) of coal (90 < 212 > mm) is mixed with reagents (total liquid volume ≤ 10 cm³) in a Teflon bomb. The Teflon bomb is placed in the microwave oven (even a domestic model may be used) and subjected to bursts of microwave energy until it is judged, usually on the basis of FTIR, that the reaction has reached equilibrium. The time required proves to be a function of the coal used, the reagents, and the solvent. These observations may be understood in terms of variation of porosity of the coal, differing steric demands of the reagents, and differing degrees of superheating of the polar solvents.

Acetylation

Acetylation³ can be achieved in two ways: (a) With ketene, CH₂=CO, a small highly reactive gas molecule which can move easily, penetrate the porous coal structure and thus give the maximum probability of complete reaction with coal -OH groups, but the substance is very toxic and long reaction times are required due to loss of reagent via ketene polymers formed on the coal preventing further reaction with hydroxyl groups. Therefore after every ten hours reaction, the ketene polymers should be removed by extraction with toluene then, after drying and weighing the coal, this procedure continues until a constant acetyl content is obtained. (b) With reagents such as acetic anhydride/pyridine, acetic anhydride/conc. H₂SO₄; acetic anhydride/CF₃CO₂O; CH₃COOH/CF₃COOH. Blom *et al.*⁴ have pointed out that acetylation of coal proceeds slowly due to steric hindrance of the -OH groups, thus long reaction times are needed for reproducible data to be obtained. Likewise the hydrolysis step may need several days refluxing with barium hydroxide prior to distillation and titration of the acetic acid. It has been shown that³ microwave heating certainly accelerates both the acetylation using the conventional reagents and hydrolysis reactions, and that greater conversions are achieved than by using the same reagents in prolonged reactions on the bench top. For example, seven days hydrolysis on the bench top produces barium silicate, which has been formed from etching the glass with weak barium hydroxide, as an undesirable side

product, but such problems are totally avoided in the microwave method. Thus not only is the microwave method more reliable in driving the reactions to equilibrium but the saving in time can also avoid unwanted reactions which are a function of the very long reaction times associated with conventional procedures.

Silylation

Even if microwave heating is used to accelerate the derivitisation and hydrolysis stages, the acetylation process is a multi-step procedure. We have developed a method based on silylation which is a "one pot" process since the silylated coal is analysed directly by quantitative ^{29}Si MASNMR methods. A range of silylation reagents is available but not all are equally effective for use in the microwave method. For studies of coals, N-(trimethylsilyl)imidazole was the preferred reagent when used in acetonitrile solution. Even with this reagent a side reaction with more tenaciously held moisture occurred to give Me_3SiOH but fortunately the presence of this material did not interfere with the analysis. A wider range of reagents could be used for the silylation of simple substituted phenols, "model compounds", although a 1:1:1 mixture of N,O-bis(trimethylsilyl)acetamide, N-(trimethylsilyl)imidazole, and trimethylchlorosilane was optimal under conditions of microwave heating.

Remarkable acceleration of reactions was achieved e.g. from 24 hours (bench) to 35 minutes (microwave) for Creswell coal, and the ultimate -OH analytical data were in excellent (Creswell) or satisfactory (e.g. Cortonwood) agreement with the definitive ketene data.⁵ (Table 1a and 1b).

The analytical method for silicon requires knowledge of the spin lattice relaxation times T_1 of silylated coals (~8s) and of appropriate standard compounds (~25s). The method requires a pulse delay of $5T_1$ (maximum) seconds between pulses, thus the accumulation time for quantitative spectra with good signal to noise ratios may be considerable. However, despite this, the time taken from commencement of analysis to result may truly be described as "rapid" in comparison with other methods.

Stannylation

Tri-n-butyltin is a much more sterically demanding reagent than is $\text{Me}_3\text{Si-}$. It is not surprising therefore that even under microwave acceleration, stannylation of 2,6-di-t-butylphenol does not occur, whereas, by contrast, reaction with 2,6-dimethylphenol occurs readily. The less sterically demanding (smaller cone angle) $\text{Me}_3\text{Sn-}$ group will react with more hindered phenols e.g. 2,6-diphenylphenol; the product, 2,6- $\text{Ph}_2\text{C}_6\text{H}_4\text{OSnMe}_3$, having been confirmed by single crystal X-ray crystallography.

The use of the triorganotin chlorides, R_3SnCl ($\text{R}=\text{Me}$, n-Bu) was not effective for coal since microwave accelerated loss of reagent via side reactions, and loss due to volatility, occurred. More effective was the use of the oxides $(\text{R}_3\text{SnO})_2\text{O}$. The point illustrated is that microwave heating may accelerate both analytically desirable and undesirable reactions.

To date a range of coals and coal macerals has been successfully stannylated using TBTO (i.e. bis-tri-n-butyltin oxide) in conjunction with acetonitrile, usually mixed with toluene, in microwave driven experiments. Quantitative methods of analysis based on ^{119}Sn MASNMR are under development and it is hoped that the more sterically demanding n- $\text{Bu}_3\text{Sn-}$ will show a lower apparent -OH content for a given coal than that determined with $\text{Me}_3\text{Si-}$, thus enabling the proportion of more hindered -OH groups to be established.

To date preliminary qualitative ^{119}Sn MASNMR data indicate chemical shifts similar to those observed for 2,6-di-substituted-stannylated phenols in which the 2,6-substituents are of small steric demand. Thus it does appear possible that the density of -OH sites of differing degrees of steric hindrance might be mapped out by treatment of the same coal with a range of reagents of differing steric demand.

Phosphorylation

Both ^{29}Si (4.71%) and ^{119}Sn (8.45%) are of relatively low natural abundance thus the development of quantitative MASNMR methods to include phosphorus is attractive given the 100% abundance of ^{31}P and its excellence as an NMR probe.⁶ In the event the microwave acceleration of phosphorylation reactions with phosphorus(III) reagents, e.g. $\text{P}(\text{OEt})_2\text{Cl}$, produced complex mixtures both when the substrate was coal or model compounds. In addition to direct phosphorylation of -OH, four side reactions were noted:

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|-------|--|-----------------|---------------|---------------|
| (i) | oxidation | P(III) | \rightarrow | P(V) |
| (ii) | hydrolysis | P-Cl | \rightarrow | P-OH |
| (iii) | solvolysis | P-OEt | \rightarrow | P-OH |
| (iv) | $\text{ROH} + \text{EtO-P} \rightarrow \text{ROP} + \text{EtOH}$ | | | |

This rendered quantitative study impossible. Naturally, more vigorous control of reaction conditions (exclusion of oxygen and moisture) would allow greater success but this departs from the objective of devising a simple, one pot method for coal -OH determination. Ironically, there is qualitative evidence that phosphorylation could be better than silylation for identifying subtle differences in -OH environments. Indeed when coal is the substrate there is

evidence for the occurrence of all reactions (i) — (iv) above. From the spectrum of ^{31}P chemical shifts, it may be deduced that a rich variety of phosphorus environment results from the reaction of coal with reagents of the class $\text{P}(\text{OR})_2\text{Cl}$. In fact the oxidation reaction is very rapid and regardless of the initial reagent being $\text{P}(\text{III})$ or $\text{P}(\text{V})$, any $-\text{OH}$ groups on the coal which are phosphorylated contain $\text{P}(\text{V})$. An oxidation and hydrolysis of a product reagent such as $\text{P}(\text{OEt})_2\text{Cl}$ is $\text{OP}(\text{OEt})_2(\text{OH})$ and this material adheres strongly to the coal suggesting that it originates primarily from reaction with any tenaciously held coal moisture (all coal samples are dried at 105°C under N_2 over one or more hours). Thus whilst the system is not without interest chemically, the analytical usefulness is limited. It may however be noted, as mentioned above, that preliminary qualitative studies of tri-*n*-butylstannylated coals give chemical shifts consistent with stannylation of weakly hindered $-\text{OH}$ groups.

Ion Exchange

It may be noted that the ability of microwave heating to accelerate the ion exchange of clay minerals² may also be exploited in coal science to afford transition metal exchanged $-\text{OH}$ groups (e.g. Ni^{2+}) which are suitable for preliminary study by EXAFS to provide some information about average $-\text{OH}$ environments.

Attempts may be made to exchange the weakly acidic sites directly, or alternatively, prior conversion to the potassium derivative may be employed. Selection of salts of copper(II) can lead to complex chemistry and ill defined products. With nickel(II) and cobalt(II) cleaner reactions could be obtained. Thus microwave derivitisation has once again proved useful in developing materials for physical study by a method (EXAFS) which may give information about the average environment of $-\text{OH}$ groups in a given coal.

Conclusions

Microwave heating will not necessarily accelerate only a reaction of particular analytical interest, the rates of side reactions may also be accelerated. If the method is to be used to derivitise $-\text{OH}$ groups it is desirable to select reagents with either no or with a minimum of side reactions. If that condition can be fulfilled, as it usually is if the reagent is selected from group 14, in our view microwave heating is now the preferred method for such derivitisation reactions.

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Table 1 (a)
Quantitative ^{29}Si MASNMR
determination of $\text{OOH}/\text{O}_{\text{Total}}$

$\text{OOH}/\text{O}_{\text{Total}}$ Quantitative ^{29}Si MASNMR				
Coals	%C	%O	$\text{OOH}/\text{O}_{\text{Total}}$ % by Silylation	Reaction Time
Gedling	81.6	9.4	41	2h
Ollerton	82.6	7.5	55	2h
Linby	83.0	8.7	61	2h
Creswell	84.5	5.9	91	35 mins.
			92	2h
Cortonwood	87.2	3.9	84	3h
Cwm	90.3	2.9	—	5h
Cynheidre	95.2	0.9	—	5h

Table 1(b)
Acetylation data from ketene and from conventional
reagents used in the microwave oven for comparison

$\text{OOH}/\text{O}_{\text{Total}}$ % by Acetylation					
Ketene	Reaction Time	$(\text{CH}_3\text{CO})_2\text{O}/$ H_2SO_4	$(\text{CH}_3\text{CO})_2\text{O}/$ Py	$\text{CH}_3\text{COOH}/$ $(\text{CF}_3\text{CO})_2\text{O}$	$(\text{CH}_3\text{CO})_2\text{O}/$ $(\text{CF}_3\text{CO})_2\text{O}$
73	100h	53	49	47	43
59	100h	50	49	40	37
75	140h	48	50	37	33
90	125h	62 (1h) 72 (2h)	63 (1h) 65 (2h)	61 (1h) 64 (2h)	54 (1h) 54 (2h)
77	114h	83	50	78	69
55	120h	60	1.6	52	55
17	48h	117	2.5	11	23